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Title: Effect of torrefaction on physiochemical characteristics and grindability of stem wood, stump and bark

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Abstract: In this work, Norway spruce stem wood, stump and bark were torrefied in a bench scale tubular reactor at 225, 275 and 300 °C with two residence times (30 and 60 minutes). The effects of torrefaction process conditions and feedstock type on the physical properties, chemical composition and grindability of torrefied biomass samples were investigated. Furthermore, information was also obtained by conducting scanning electron microscopy (SEM) analysis to gain insights into changes of microstructure and morphology of biomass samples upon torrefaction at different conditions. Higher heating value and fixed carbon content of torrefied biomass samples increased with increased torrefaction severity. Torrefaction caused decrease of hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) atomic ratios with increasing temperature and residence time, which results in increase of energy density of torrefied biomass samples. Chemical compositions of torrefied biomass samples considerably changed with increase of torrefaction severity. For the stem wood and stump, the relative hemicellulose content significantly decreased from 42.3% and 29.8% to less than 1% after torrefaction at 300 °C for 60 minutes, respectively. The hemicellulose content of untreated bark decreased from 27.5% to 0.14% after torrefaction at the same conditions. Additionally, the cellulose content of the torrefied bark drastically decreased already to half the initial value at a torrefaction temperature of 275 °C, with only trace amounts left in the 300 °C torrefied products. The grindability of stem wood and stump were substantially improved after torrefaction treatment. The energy required for grinding stem wood and stump torrefied at 225 °C decreased to respectively 87 and 70 kwh/ton, which are less than 50% of the energy needed for grinding the untreated samples. For raw bark, much less grinding energy is required compared to those for raw stem wood and stump, and torrefaction has minor effects on the grindability of bark. The ground torrefied biomass samples have much smaller particles than those of the untreated ones. The improvement of grindability of torrefied biomass samples can be coupled to the weakening of the fibre bonds indicated by change in chemical compositions. SEM analysis results show that particles from ground torrefied samples lose

their fibrous structure with decrease of length-to-diameter ratios, compared to untreated biomass samples. It explains the shift in particle size distribution curves towards smaller particles as obtained from the sieving tests.

Effect of torrefaction on physiochemical characteristics and grindability of stem wood, stump and bark

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Abstract

In this work, Norway spruce stem wood, stump and bark were torrefied in a bench scale tubular reactor at 225, 275 and 300 °C with two residence times (30 and 60 minutes). The effects of torrefaction process conditions and feedstock type on the physical properties, chemical composition and grindability of torrefied biomass samples were investigated. Furthermore, information was also obtained by conducting scanning electron microscopy (SEM) analysis to gain insights into changes of microstructure and morphology of biomass samples upon torrefaction at different conditions. Higher heating value and fixed carbon content of torrefied biomass samples increased with increased torrefaction severity. Torrefaction caused decrease of hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) atomic ratios with increasing temperature and residence time, which results in increase of energy density of torrefied biomass samples. Chemical compositions of torrefied biomass samples considerably changed with increase of torrefaction severity. For the stem wood and stump, the relative hemicellulose content significantly decreased from 42.3% and 29.8% to less than 1% after torrefaction at 300 °C for 60 minutes,

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34 distribution curves towards smaller particles as obtained from the sieving tests.

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36 **Keywords:** stem wood, stump, bark, torrefaction, grindability, chemical composition
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41 **Highlights:**

- 42
- 43 • Comparative study of torrefied stem wood, stump and bark of Norway spruce
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- 45 • Changes in chemical composition and grindability of torrefied samples
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- 47 • Principal component analyses reveal statistical correlations between grindability
- 48 and chemical compositions
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- 51 • SEM analyses show torrefied sample particles having lower length-to-diameter
- 52 ratios
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1 Introduction

Adoption and utilization of renewable energy sources are important for the modern society, considering the ever increasing energy demands and severe global warming due to use of fossil fuels. In future energy scenarios, biomass will play an important role in the energy supply [1]. A wide range of energy products can be produced from biomass via thermochemical conversion and biological conversion routes, which can be in the form of solid (bio-solid), liquid (bio-oil) or gas (bio-gas or syngas) [2]. Therefore, biomass is a flexible energy source that can be converted into various energy products to meet different demands. Norway has abundant forest resources and more than 40% of the land is covered by forest [3]. Biomass materials from the forest has a great potential to provide suitable feedstocks for bioenergy.

However, further development of bioenergy and utilization of biomass in a large scale have been hindered by limitations of the biomass as solid fuel. These limitations are mainly related to physical and chemical properties of the biomass [4, 5]. Compared to coal, biomass materials normally have low bulk density, poor grindability, low calorific value, high moisture content and hydroscopicity [6]. These limitations greatly affect the conversion efficiency of biomass materials into energy. In addition, the whole biomass-to-energy value chain is considerably impacted by these limitations due to costly storage, handling and transportation of biomass [7, 8]. Among many pretreatment technologies, torrefaction of biomass has gained continuous interests in the past decade [1, 5, 6, 9, 10]. Torrefaction is usually conducted in inert atmosphere at a temperature range from 200 to 300 °C, driving out the moisture, and parts of the volatile organic compounds in the biomass [1, 11]. Torrefied biomass retains most of the chemical energy in the raw biomass materials. Upon torrefaction, biomass can be ground easily into small particles with higher shape uniformity and sphericity [12-14]. This is mainly due to reduction of moisture content and change of chemical compositions of the raw biomass during torrefaction [10, 15, 16]. Torrefied biomass with unique properties are more suitable for logistics and further conversion to energy. Key torrefaction process parameters include temperature, residence time, pressure, gas atmosphere and heating rate [1]. These

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4 parameters have critical effects on torrefaction behaviour, distribution and properties of
5 torrefaction products and the overall energy and mass conversion efficiency [17]. On the
6 other hand, the characteristics of biomass materials will also play an important role in the
7 torrefaction process.
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11 During harvesting and thinning of forest, stem wood is a main product with residues such
12 as tops and branches as well as the stumps left behind in the forest. It has been reported
13 that stump constitute 22-24% of the stem volume of a mature conifer tree, representing a
14 very significant bioenergy potential [18, 19]. A vast amount of bark is generated as the
15 stem wood is debarked before further utilization for pulp and paper and timber products
16 production [20]. Both stump wood and bark are still underutilized resources and have a
17 great potential for energy production. In comparison to stem wood, the bark and stump
18 are more difficult to use due to several drawbacks as solid fuel as mentioned above [21,
19 22]. Torrefaction is a promising technology to upgrade bark and stump into high quality
20 solid fuels with more uniform properties. Until now, the biomasses subjected to
21 torrefaction studies have mainly been stem wood from different wood species,
22 agricultural wastes, short rotation coppice and algae [1, 13, 14, 16, 23-29]. Very little
23 research has been carried out to investigate torrefaction behaviours of bark and stump
24 from trees and the properties of their torrefied solid counterparts [22, 27]. In addition,
25 previous studies have focused on the effect of process conditions on the mass yield and
26 energy yield of biomass upon torrefaction treatment and thermal conversion behaviours
27 of torrefied biomass [10, 14, 17, 28, 30]. Less attention has been given to the change of
28 chemical composition of solid torrefied biomass. To the best of our knowledge, this is the
29 first work reporting chemical composition analysis of untreated and torrefied stumps.
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33 The present work focuses on studying effects of torrefaction on the physiochemical
34 properties and grinding energy consumption of woody biomasses including stem wood,
35 stump and bark from Norway spruce.
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2 Materials and Methods

2.1 Biomass materials

In the present work stem wood, stump and bark from Norway spruce (*Picea abies*) were investigated. The Norway spruce trees harvested in South Norway were divided into three parts including trunk (with bark), stump and tops and branches. The trunk wood was debarked to get stem wood and bark. The stem wood was cut into strips and further into cubes with sides of 1 cm. The stump was shredded into chips and those with size of 3-5 cm were subjected to further experiments. The bark was chipped into pieces and the pieces with size of 5-7 cm were used. The stem wood cubes, bark and stump chips were dried at 105 °C for 24 hours for further analysis and torrefaction experiments.

Table 1 Properties of the untreated woody biomass (dry basis).

Sample	Stem wood	Stump	Bark
Volatile matter content (wt %, db)	88.12	86.69	74.85
Ash content (wt %, db)	0.31	0.41	2.11
Fixed carbon content (wt %, db)	11.57	12.90	23.04
K (mg/kg, db)	272	245	2011
Ca (mg/kg, db)	1030	1235	7803
Na (mg/kg, db)	22	36	47
Si (mg/kg, db)	82	253	3602

As can be seen from Table 1, the stump has similar properties as those of the stem wood. The fixed carbon content of the stump is 1.3% higher than that of the stem wood. On the other hand, the bark contains as much as 23.0% fixed carbon, but also 2.1% ash. Compared to stem wood and stump, contents of inorganic elements in bark are significantly higher as shown in Table 1, the stump has similar properties as those of the stem wood.

2.2 Torrefaction experiments

The torrefaction experiments were conducted in a bench-scale tubular reactor. It includes a tubular vessel, an electrical gas pre-heater with a temperature controller, a condensate receiver and a gas supply system. For one torrefaction experiment, around 80 grams of

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4 untreated biomass sample was first loaded into the vessel. After sample loading, the
5 tubular vessel was closed tightly and connected with the gas supply system and the
6 condenser. The tubular vessel was then placed inside an electrically heated furnace and
7 the temperature in the furnace is monitored by three thermocouples located on the top,
8 middle and bottom of the furnace. The tubular vessel is continuously purged with 1 L
9 min⁻¹ nitrogen to eliminate presence of oxygen, thereby avoiding possible oxidization and
10 ignition of the sample inside. The sample was heated up at a heating rate of 15 °C/min to
11 three final temperatures (225, 275 and 300 °C). The residence time for one sample at
12 each final temperature was 30 and 60 minutes, respectively. After each torrefaction
13 experiment, the reactor was cooled down to room temperature with continuous purge of
14 the nitrogen. The cooled torrefied biomass materials were discharged and weighted to
15 determine the solid yield. The mass yield of one torrefaction experiment was calculated
16 as the percentage of initially loaded pre-dried biomass sample, as follows:
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$$mass\ yield = \left(\frac{m_{torrefied}}{m_{untreated}} \right) \times 100$$

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35 Then the torrefied biomasses were loaded in airtight plastic bags and stored in a
36 desiccator for further studies. [10]
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40 2.3 Fuel characterization 41

42 The untreated and torrefied biomass were subjected to proximate analysis. The volatile
43 matter and ash content were determined according to procedures described in ASTM
44 Standard E 872 and D1102. The fixed carbon content is calculated by difference from
45 one hundred and the sum of volatile matter and ash content. The C, H, N and S contents
46 were measured by employing an elemental analyzer (Eurovector EA 3000 CHNS-O
47 Elemental Analyser). The oxygen content is calculated by difference. For each sample,
48 the proximate and elemental analysis was repeated 3 to 5 times respectively and average
49 values of these measurements are presented. The gross calorific value of ground
50 untreated and torrefied biomasses was measured by using an adiabatic oxygen bomb
51 calorimeter (IKA C2000 calorimeter) based on ASTM Standard D 5865-03. For each
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4 measurement, around 1 gram of sample was loaded in a glass crucible and combusted
5 inside the bomb calorimeter surrounded by a water jacket. After ignition by a pure cotton
6 thread in pure oxygen, the sample start to burn and released heat that is transferred to the
7 water jacket causing the temperature to increase. The higher heating value of one sample
8 was calculated based on the increase in temperature and expressed in MJ/kg. Based on
9 the mass yields and higher heating values, energy density and energy yield for a sample
10 torrefied at different conditions can be calculated as follows:
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$$18 \text{ Energy density} = \frac{HHV_{torrefied}}{HHV_{untreated}} \quad (2)$$

$$19 \text{ Energy yield} = \text{mass yield} \times \left(\frac{HHV_{torrefied}}{HHV_{untreated}} \right) \times 100 \quad (3)$$

20 21 22 23 24 25 26 2.4 Chemical composition analysis

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28 For untreated and torrefied biomass samples, the contents of carbohydrates were analysed
29 according to the slightly modified method reported by Sluiter et al [31]. The untreated
30 and torrefied biomass samples were milled to particles smaller than 1 mm and digested
31 by a two-step acid hydrolysis. The samples were treated with 72% H₂SO₄ for 2 hours at
32 room temperature, and then with 4% H₂SO₄ for 1 hour at 121 °C. The suspensions of
33 each digestion product were filtered and washed by distilled water through gas filter
34 crucibles. The sugar concentrations (glucan, mannan and galactan) of the filtered
35 supernatants were analysed with high performance liquid chromatography (HPLC) using
36 an Agilent 1260 system with a Hi-Plex H column (Agilent, CA, USA) at 65 °C. An
37 eluent of 5mM H₂SO₄ was used at a flow rate of 0.5 mL min⁻¹. The solid residues
38 remaining after washing were dried at 105 °C until reaching a constant weight. This
39 fraction contains the acid-insoluble organics and ash. The dry solid residues were heated
40 at 550 °C for 5 hours in air to determine the content of acid-insoluble ash. The Klason
41 lignin content was calculated by deducting the acid-insoluble ash content from the dried
42 acid-insoluble residue content. All experimental data were determined using three
43 replicates.[10]
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2.5 Grindability test

The grindability of the raw and torrefied biomass samples was assessed by grinding them in a cutting mill (IKA MF 10.1). The grinding of one sample included two stages: pre-grinding and fine grinding. In the pre-grinding stage, a known quantity of stem wood cubes and bark and stump chips with and without torrefaction treatment were fed into the cutting mill without a bottom sieve to reduce their sizes. The smaller pieces and grains produced from the pre-grinding stage were used for further fine grinding. Fine grinding of the products from the pre-grinding stage was carried out in the same cutting mill equipped with a 1 mm bottom sieve. The cutting mill motor was equipped with a circuit breaker to avoid possible motor overloading. The electricity consumed during the pre- and fine grinding stages was monitored by a digital wattmeter (Paladin 256-TWKW from Cromptan Instruments), which was connected to computer for recording instantaneous power consumption every 2 seconds. The power consumption for an empty load was also recorded before each grinding stage with sample loaded into the mill. The empty load was subtracted from the each grinding test in order to obtain the energy requirements for grinding the biomass. The specific energy consumption required for grinding was calculated by integrating the area below the instantaneous power consumption curve (watt-seconds) with respect to time required for grinding the given amount of sample. For one sample, the integrated values from both the pre-grinding and fine grinding stage were summed to obtain the total power consumption. The energy consumption required for grinding one sample is expressed per unit mass for comparison purpose. The powder samples produced in the fine grinding stage were sieved by a vibrating sieving machine (Fritsch Analysette 3 Pro) with the following mesh sizes: 1 mm, 0.5 mm, 0.3 mm, 0.2 mm, 0.1 mm and 0.063 mm. The sample particles collected from the different sieves were weighed and presented as a percentage of the initial sample mass.

2.6 PCA analysis

Principal component analysis (PCA) using Statistica 12 software (StatSoft, Inc. Tulsa, Oklahoma, USA) was employed due to the large number of samples and experimental data. PCA has been used to reveal correlations between the chemical composition data and the particle size distribution of the untreated and torrefied samples. The aims of a

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4 PCA analysis are to identify patterns in data and finding patterns to decrease the data
5 dimensionality with minimal loss of information. The factors (principal components) are
6 the linear combinations of the original measured variables. The principal components
7 describe different percentages of the total variance; usually two or three factors are
8 enough to explain the differences between the studied samples. The results can be
9 presented in the score plots, which denote the samples in the space of two principal
10 components. Factor loadings show the correlation between the original data and the
11 principal components.
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20 2.7 SEM analysis

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22 Scanning electron microscopy analysis was carried out to investigate microstructure and
23 morphology of untreated and torrefied biomass materials. The ground untreated and
24 torrefied biomass particles with size in the range of 0.6-1 mm and smaller than 0.063 mm
25 were examined by scanning electron microscopy (Zessia Ultra, 55 Limited Edition). The
26 sample particles were spread on an adhesive carbon tape fastened on a sample tab and
27 sent into the SEM for scanning. The SEM was operated with the same parameters for
28 particles in the same size range, which are from untreated and torrefied biomasses.
29 Therefore, the SEM images are comparable for the sample particles in terms of size,
30 shape and morphology.
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40 3 Results and Discussion

41 3.1 Torrefied biomass mass and energy yields

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43 Table 2 shows the mass yield, energy yield, energy density and HHV of the torrefied
44 samples as a function of the final temperature and residence time. Mass yields of stem
45 wood, stump and bark decreases with increase in torrefaction temperatures as shown in
46 Table 2. As the torrefaction temperature increased to 275 °C, there are significant mass
47 losses for the three studied biomass materials. The mass yields of all three studied
48 biomass materials drop continuously with further increase of torrefaction temperature to
49 300 °C. Compared to stem wood and bark, the stump is more sensitive to increase of the
50 torrefaction temperature. The yields of solid dramatically declines from above 90% to 46-
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55% as the torrefaction temperature increase from 225 °C to 300 °C. The mass yields decrease with increase of residence time as shown in Table 2. However, torrefaction time gave less significant effect than temperature on mass yields for all experiments conducted at 225 and 275 °C. On the other hand, at the torrefaction temperature 300 °C, the mass yields of stem wood and stump were considerably affected by the increase in torrefaction time, which was reduced by about 11.1% and 9.4%, respectively, when the torrefaction time was increased from 30 to 60 minutes. Table 2 shows that HHV of torrefied biomass materials increased with raise in torrefaction temperature and time. The HHV values increased from 19.51-19.89 MJ kg⁻¹ for the untreated biomass to 23.38-24.35 MJ kg⁻¹ for those torrefied at 300 °C. The highest increase of HHV was observed for bark, which increase from 19.51 MJ kg⁻¹ to 24.35 MJ kg⁻¹. With increase of torrefaction temperature from 225 increased to 300 °C, the energy yield of the torrefied samples decreased from 93.05% to 55.63% as shown in Table 2. Although torrefaction under severe conditions produces torrefied biomass with higher HHV, a large amount of energy was lost due to loss of sample mass upon torrefaction, explaining the decrease of the energy yield shown in Table 2. The energy density of torrefied stem wood, bark and stump was enhanced with increase of torrefaction temperature and time.

Table 2 Mass and energy yield, energy density and HHV of torrefied biomass (dry basis).

Biomass	Mass yield (%)	HHV (MJ kg ⁻¹)	Energy yield (%)	Energy density
Untreated stem wood	100	19.75	100.00	1.00
225°C-30 min	92.4	20.03	93.05	1.01
225°C-60 min	91.2	20.11	92.20	1.01
275°C-30 min	79.3	21.06	83.95	1.07
275°C-60 min	75.7	21.28	80.99	1.08
300°C-30 min	68.6	23.16	79.88	1.17
300°C-60 min	57.5	23.61	68.27	1.20
Untreated stump	100	19.51	100.00	1.00
225°C-30 min	92.7	19.84	94.26	1.02
225°C-60 min	90	20.15	92.96	1.03
275°C-30 min	71.6	20.50	75.24	1.05
275°C-60 min	69.4	20.81	74.02	1.07

300°C-30 min	55.6	22.72	64.76	1.16
300°C-60 min	46.2	23.49	55.63	1.20
Untreated bark	100	20.14	100.00	1.00
225°C-30 min	90.4	21.11	96.93	1.05
225°C-60 min	81.5	21.33	88.30	1.06
275°C-30 min	72.5	22.47	82.74	1.12
275°C-60 min	68.5	23.02	80.08	1.14
300°C-30 min	63.0	23.38	74.80	1.16
300°C-60 min	60.5	24.35	71.83	1.21

3.2 Characterization of untreated and torrefied biomass

Table 3 shows a summary of proximate and ultimate analyses of the untreated and torrefied biomass samples. The volatile matter content of torrefied biomasses decrease with increase of torrefaction severity. At a temperature of 225 °C, the volatile matter content of all torrefied biomasses slightly decreased, while significant reduction was observed at temperatures of 275 °C and 300 °C. The ash content of torrefied biomasses increased due to loss of organic matter during torrefaction. Similar changes of proximate analysis results were also found in studies on torrefied pine, birch, logging residues and other woody biomass species [10, 27-30, 32].

Table 3 Proximate and ultimate analysis of untreated and torrefied biomass samples

Sample	VM (% db)	Ash (% db)	FC (% db)	C (% daf)	H (% daf)	N (% daf)	S (% daf)	O (% daf)
Untreated stem wood	88.12	0.31	11.57	48.78	6.27	0.17	0.05	44.73
225°C-30 min	87.90	0.33	11.77	50.06	6.14	0.05	0.03	43.72
225°C-60 min	85.42	0.39	14.19	50.46	6.09	0.06	0.03	43.36
275°C-30 min	78.52	0.41	21.07	54.08	5.98	0.07	0.02	39.85
275°C-60 min	74.36	0.42	25.22	55.14	5.87	0.08	0.02	38.89
300°C-30 min	62.89	0.46	36.65	62.17	5.72	0.14	0.01	31.96
300°C-60 min	58.65	0.49	40.86	64.21	5.54	0.16	0.01	30.08
Untreated stump	86.69	0.41	12.90	47.38	6.49	0.11	0.03	45.99
225°C-30 min	84.61	0.67	14.72	49.21	6.21	0.06	0.02	44.50
225°C-60 min	82.12	0.66	17.22	50.56	6.11	0.07	0.02	43.24
275°C-30 min	75.22	0.60	24.17	52.02	6.02	0.08	0.02	41.86
275°C-60 min	73.34	0.66	26.6	53.21	5.98	0.10	0.01	40.70
300°C-30 min	65.66	0.77	33.66	60.21	5.89	0.11	0.01	33.78
300°C-60 min	55.74	1.08	43.19	63.25	5.76	0.13	0.01	30.85

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Untreated bark	74.85	2.11	23.04	49.09	6.06	0.45	0.05	44.35
225°C-30 min	71.21	2.38	26.41	55.40	5.53	0.53	0.03	38.51
225°C-60 min	68.10	2.87	29.02	56.47	5.41	0.57	0.03	37.52
275°C-30 min	63.45	2.65	33.90	61.01	5.20	0.62	0.02	33.15
275°C-60 min	60.97	2.50	36.52	63.76	4.86	0.65	0.01	30.72
300°C-30 min	53.10	3.05	43.95	67.34	3.89	0.67	0.01	28.09
300°C-60 min	47.94	4.13	47.93	68.86	3.25	0.71	0.01	27.17

As shown in Table 3 the elemental composition of torrefied biomasses also change as a function of torrefaction severity. As the torrefaction temperature increases from 225 °C to 300 °C, the elemental carbon content of the stem wood increased from 50.1% to 64.2%, whereas the elemental hydrogen content decreased from 6.1% to 5.5%. Moreover, more pronounced increases of elemental carbon and reduction of elemental hydrogen content were observed from the torrefied bark. Changes in elemental compositions of the torrefied biomass are illustrated in a Van Krevelen diagram in Fig. 1. Both atomic H/C and O/C ratios decrease with increase of torrefaction severity. The torrefied bark had generally smaller H/C and O/C ratios compared to those of torrefied stem wood and stump. A similar decreasing of atomic H/C and O/C ratios of torrefied biomasses have been reported in previous studies [17, 23, 28, 32]. During torrefaction, conversion of biomass is mainly associated with dehydration, decarboxylation and depolymerisation of the organic portion of the biomass, resulting in loss of water and release of gases and light volatiles [5]. Therefore, during torrefaction, the biomass loses relatively more oxygen and hydrogen compared to carbon. Due to change of content of elemental carbon, hydrogen, and oxygen, the heating value of the torrefied biomass increase consequently, as shown in Table 2.

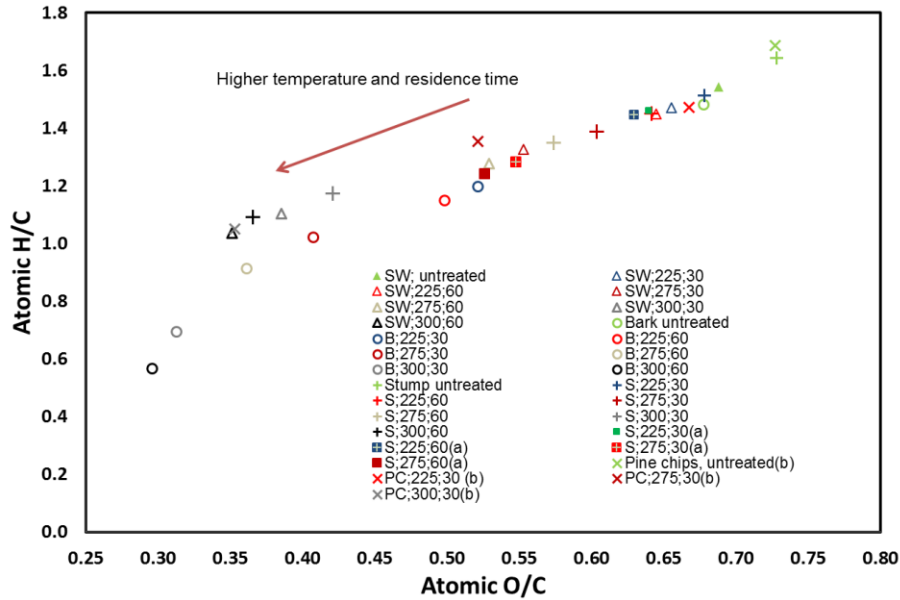


Fig. 1. Van Krevelen plot of atomic H/C versus atomic O/C for untreated and torrefied biomass, (a) data from reference [28] , (b) data from reference [10].

3.3 Compositional analysis of raw and torrefied samples

Compositional analysis of raw and torrefied biomass samples was carried out to follow the decomposition of the lignocellulose polymeric components and understand the conversion behaviour of the samples during torrefaction. The results are presented in Fig. 2. The Klason lignin contains the acid insoluble residue of the samples without the acid insoluble ash. The glucan content of the samples mostly characterizes the cellulose fraction of the biomass, whereas the sum of the mannan and galactan content represents the hemicellulose fraction of the samples. The fraction named “Other” represents all undetermined components such as extractives, acid soluble lignin and acid soluble minerals. To provide a comprehensive comparison of the raw and treated samples, the weight loss of the torrefied samples during torrefaction is presented in Fig. 2. As shown in Fig. 2, untreated bark has the highest Klason lignin content (40.8%). The untreated stump has the highest hemicellulose content (23.4%), while the untreated stem wood has the highest cellulose content (42.5%). The lignocellulose content (sum of lignin, cellulose and hemicellulose) of the untreated stem wood is 89.9%, while that of the untreated stump and bark is 80.5% and 77.9%, respectively. The reason for the relatively lower

lignocellulose content of stump and bark could be their higher extractives, acid soluble lignin and acid soluble mineral content.

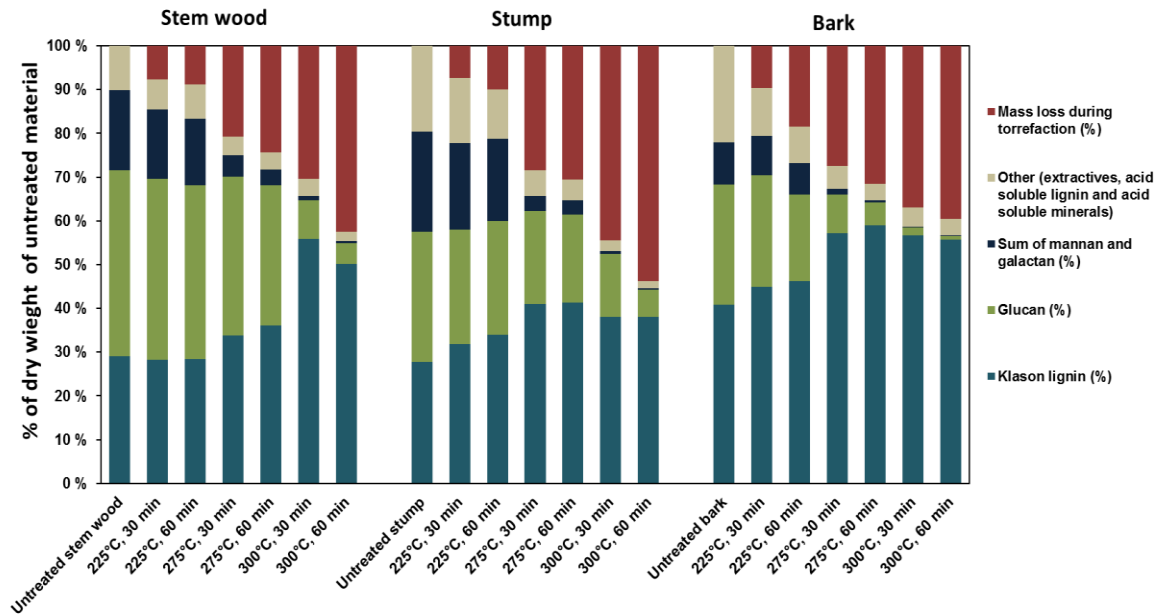


Fig. 2. Composition of untreated and various torrefied stem wood, stump and bark (dry basis).

The alkali contents of the raw samples have been determined using ICP-OES (Table 1). The raw stem wood and stump contain around 250-300 mg/kg potassium and around 1000 mg/kg calcium, while both the potassium and calcium content of the raw bark is about seven times higher than that of the stem wood and stump. During torrefaction, lignocellulose materials decompose to different degrees upon torrefaction severity [33, 34]. The decrease of both glucan and the sum of mannan and galactan reflects decomposition of cellulose and hemicellulose in the samples. As Fig. 2 shows, hemicellulose (measured as the sum of mannan and galactan) is the least thermally stable component of the studied biomass samples during torrefaction. About 20% of the hemicellulose content of the samples decompose up to 225 °C for each of the studied samples. After torrefaction at 275 °C, the relative amount of the hemicellulose in the bark samples drastically decreases, while stem wood and stump have about one fifth of the hemicellulose content of the raw sample. The hemicellulose content of them further decrease and only a minor fraction was measured for samples torrefied at 300 °C. The bar diagram also shows that the content of cellulose - indicated by the content of glucan - does not decrease evidently even at the torrefaction temperature 275 °C for stem wood

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4 and stump, while a significant decrease (more than 80 %) is observed for bark at this
5 temperature. At 300 °C torrefaction temperature, the residence time has a significant
6 effect on the cellulose decomposition. After torrefaction at 300 °C for 30 and 60 minutes
7 the cellulose content of the stump sample decreased to 48 and 21% of the cellulose
8 content of the raw material, respectively, whereas that of stem wood decreased to only 20
9 and 11%, respectively. These observations may point to that the thermal stability of
10 cellulose in the bark sample is lower compared to the stem wood and stump samples. The
11 bark sample has more than an order of magnitude higher alkali content than stem wood
12 and stump (Table 1). The alkali metals are known to exert a great influence on the
13 thermal decomposition of cellulose [22, 34-36]. The change in the chemical compositions
14 of the studied samples confirmed that the alkali metals have catalytic effects on the
15 cellulose decomposition during thermal treatment in this temperature range. As the bar
16 diagram presents, the Klason lignin content of the torrefied samples increase considerably
17 with increasing torrefaction temperatures. The Klason lignin contains all acid insoluble
18 components of the sample, excluding ash. During torrefaction, certain fractions of the
19 polysaccharides, acid soluble lignin and extractives were probably transformed into acid
20 insoluble carbonaceous products by cross-linking and charring reactions [12, 22]. The
21 increasing torrefaction temperature support these reactions, resulting in the greater
22 amount of Klason lignin content at higher temperatures.
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40 3.4 Effect of torrefaction on grindability

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42 Fig. 3 shows the total energy required for grinding the raw and torrefied biomass samples,
43 which includes energy consumed for both the pre-grinding and fine grinding steps. For
44 stem wood and stump, the energy required for grinding the samples was reduced
45 significantly as a result of torrefaction treatment. Compared to raw stem wood and stump,
46 only about half of the energy is needed for grinding the stem wood and stump torrefied at
47 225 °C. This trend is in good agreement with those reported in literatures for the grinding
48 of stem wood and stump wood [14, 19, 28]. It indicates that significant energy savings
49 associated with size reduction can be achieved by torrefying stem wood and stump, even
50 at a mild torrefaction condition. The change of energy required for grinding untreated and
51 torrefied biomasses can be linked to decomposition of polymeric components of the
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4 studied biomasses during torrefaction. For a woody plant, the plant cell wall is tough
5 layer protecting the plant structure against mechanical stress [12]. In the cell wall, the
6 cellulose microfibrils and macrofibrils are linked or embedded in a matrix of disoriented
7 hemicellulose to form a cellulose-hemicellulose network [5, 37]. The cell wall with such
8 a microstructure provides high strength and tenacity, making the plant mechanically
9 strong [1]. Therefore, the wood has anisotropic and fibrous nature, which makes grinding
10 of wood energy intensive and makes it difficult to obtain fine particles. During
11 torrefaction, continuous decomposition of hemicellulose causes weakening and
12 destruction of the highly interlinked cellulose-hemicellulose matrix which can no longer
13 capable to support the cellulose fibres [12]. At a high enough torrefaction temperature,
14 both hemicellulose and cellulose decompose more intensively into volatiles and char-like
15 brittle solid [37]. This results in loss of tenacity and mechanical strength of cell walls and
16 wood structure consequently. Hence, the energy requirement for grinding torrefied wood
17 into small particles is significantly reduced. As shown in Fig. 2, both the hemicellulose
18 and cellulose content in the stem and stump wood considerably decreased with increase
19 of torrefaction severity. It partially explains the reduction of the energy requirements for
20 grinding the torrefied stem wood and stump. Compared to stem wood and stump, much
21 less energy is needed for grinding the untreated bark. In addition, the torrefaction
22 treatment has minor effects on the energy consumption for grinding bark, although that of
23 the hemicellulose and cellulose were considerably reduced. It might be due to differences
24 in content and nature of lignocellulose compositions (hemicellulose, cellulose and lignin)
25 and the integrated structure of the compositions of the bark compared to the stem wood
26 and stump. Similar differences in grindability have been observed for coniferous and
27 deciduous wood [12]. Torrefied coniferous wood predominately consisting of mannan-
28 based hemicellulose has poorer grindability compared to deciduous wood mainly
29 consisting of xylan-based hemicellulose [32].
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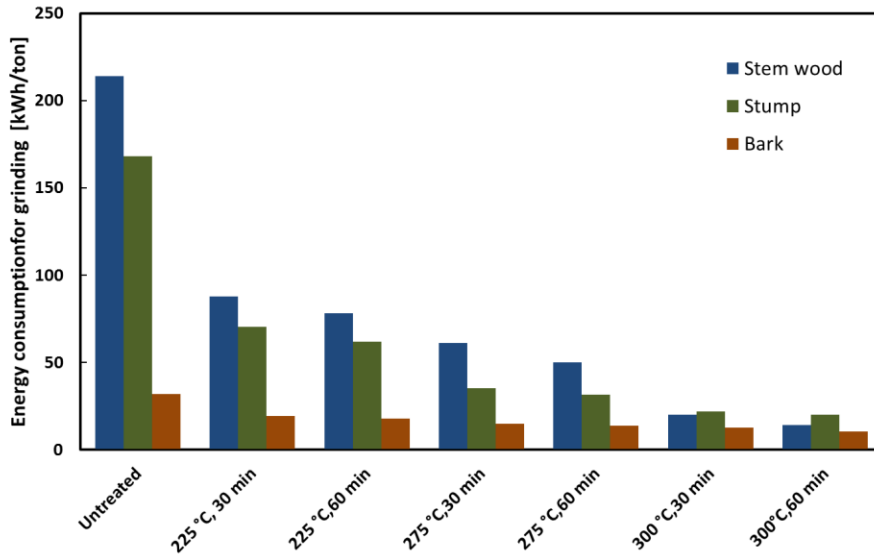


Fig. 3. Energy required for grinding raw and torrefied samples.

Fig. 4 shows the effect of torrefaction severity on size distribution of particles passing varying sieves with different cut-sizes. In general, torrefaction temperature and residence time have considerable influences on percent of particles in the various size ranges. It can be seen that 42 wt % and 25 wt % of respectively ground untreated stem wood and stump are large particles in the size range of 0.5 to 1 mm. After torrefaction at 225 °C, the amount of particles with such size significantly decreased to 18-20 wt % and 10-12 wt %, respectively. With further increase of torrefaction severity, the percent of particles in same size range further decrease and only a small amount was obtained as the stem wood and stump were torrefied at 300 °C. In addition, the amount of particles with smaller sizes was also significantly increased for stem wood and stump torrefied at a higher temperature. In comparison, increasing the torrefaction residence time gave only a slight increase in the amount of particles with smaller sizes. As shown in Fig. 4, the particle size distribution of untreated and torrefied bark are quite different from those of stem wood and stump. For the untreated bark, the percentage of large particles ($0.5 \text{ mm} < d < 1 \text{ mm}$) is sustainably small, in comparison to stem wood and stump. The major fraction of the untreated bark particles has a size in the range of $0.3 \text{ mm} < d < 0.5 \text{ mm}$, which decreases evidently after torrefaction treatment. Moreover, the percentage of fine bark particles ($d < 0.063 \text{ mm}$) increases considerably upon the increase of torrefaction temperature. Fig. 5 shows cumulative particle distribution curves of ground untreated and

torrefied biomass samples. The particle size distribution curves clearly shift towards smaller particles. Similar changes of particle size distribution of ground biomass have been reported in other studies [10, 21]. As mentioned already, torrefaction of biomass causes decomposition of hemicellulose and breakdown of the hemicellulose-cellulose interlinked matrix. It makes grinding of torrefied wood much easier with production of more small particles.

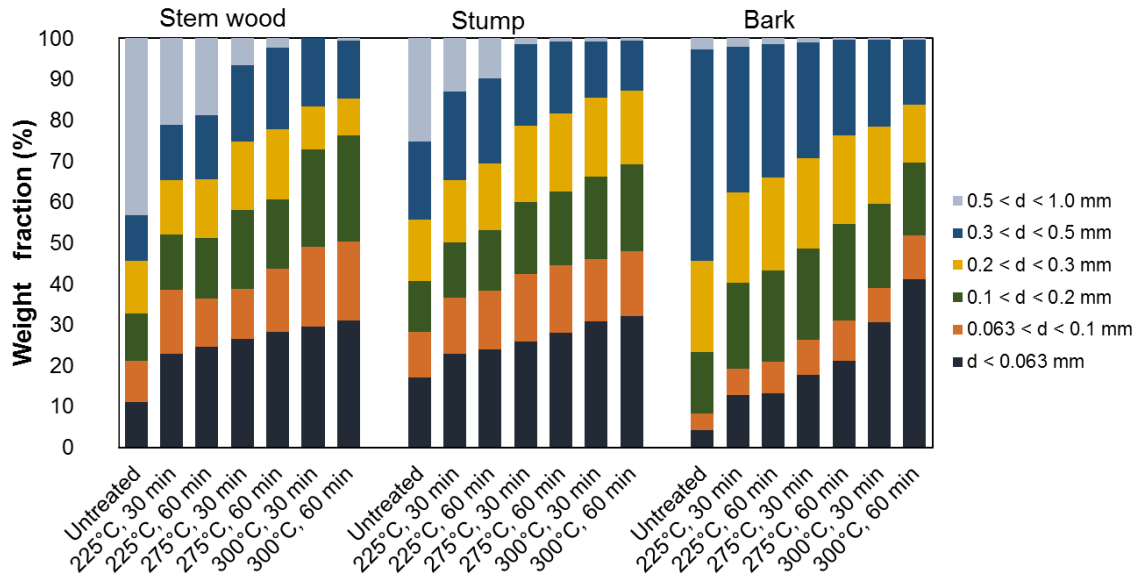
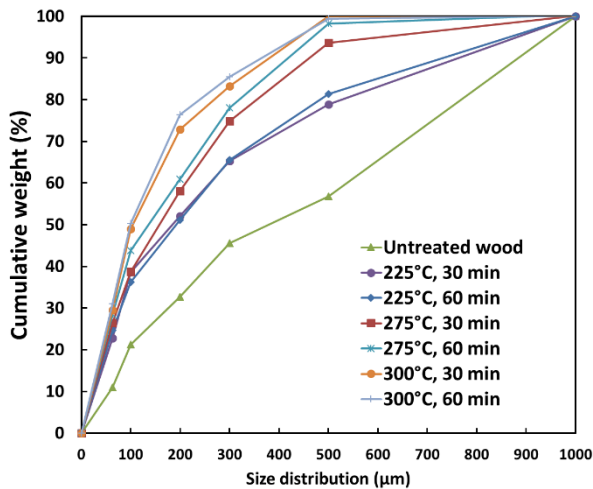


Fig. 4. Particle size distributions for the stem wood, stump and bark as a function of torrefaction severity



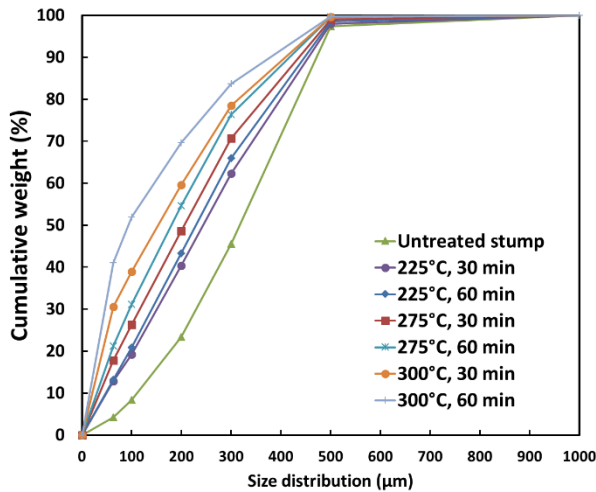
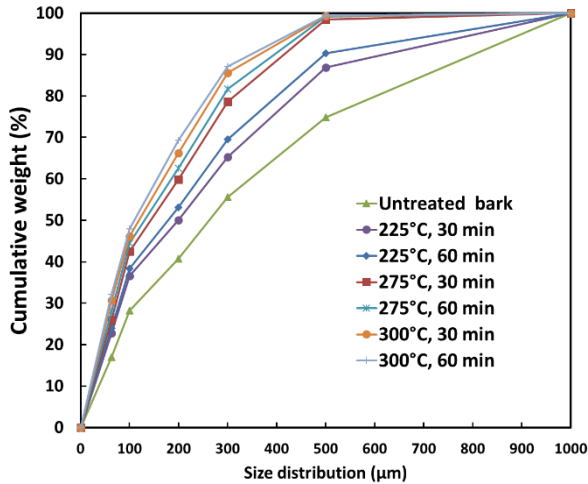


Fig. 5. Cumulative particle size distributions for the stem wood, stump and bark as a function of torrefaction severity

3.5 PCA calculation based on chemical composition and particle size distribution as a function of torrefaction severity

Principal component analysis (PCA) has been applied to find statistical correlations between the chemical composition data (Fig. 2) as well as the particle size distribution (Fig. 4) of the ground raw and torrefied samples. In the PCA calculation, the first principal component (Factor 1) described 53.13% of the total variance and the second component (Factor 2) described 27.36% of the total variance, these two factors are adequate to characterize the major differences between the studied samples. In the score plot (Fig. 6a) it can be seen that the behaviour of the bark samples during torrefaction

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4 clearly differ from the stem wood and stump samples. Factor 1 differentiates the raw, the
5 mildly and the severely torrefied samples. As a function of the Factor 2, the stem wood
6 and stump samples are found in the upper, and the bark samples in the lower part of the
7 score plot. This difference is probably due to the different cellulose, hemicellulose, lignin,
8 and extractive content of the samples; which is reflected in the different particle size
9 distribution of the ground samples.
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16 The loading plot (Fig. 6b) shows that the values of glucan, sum of mannan and galactan
17 content and the “Other” part of the chemical composition (which contains extractives,
18 acid soluble lignin and acid soluble minerals) correlate negatively with the mass loss and
19 the Klason lignin content of the samples. Factor 1 is composed of mainly these
20 parameters and mostly separates the samples as a function of the torrefaction severity.
21 Particle size distribution data is reflected mainly in Factor 2. The raw bark has
22 significantly higher extractives and Klason lignin content than that of the raw stem wood
23 and stump, which may contribute to the different particle size distribution of the raw
24 samples. For the raw bark, the percentage of fine particles ($d < 0.1$ mm) and large
25 particles ($0.5 \text{ mm} < d < 1$ mm) are quite small, however the percentage of medium size
26 particles ($0.2 \text{ mm} < d < 0.5$ mm) is rather large, in comparison to raw stem wood and
27 stump. During torrefaction, the moisture content releases and the extractives and
28 carbohydrate content of the samples degrade, therefore the torrefied samples become
29 more brittle. Comparing the particle size distribution of the ground raw and torrefied
30 samples we can conclude, that by applying more severe torrefaction before the grinding,
31 the obtained particle size distribution of the stem wood, stump and bark sample become
32 similar. The decreasing distance of bark samples from stem wood and stump samples on
33 the score plot visualize this correlation.
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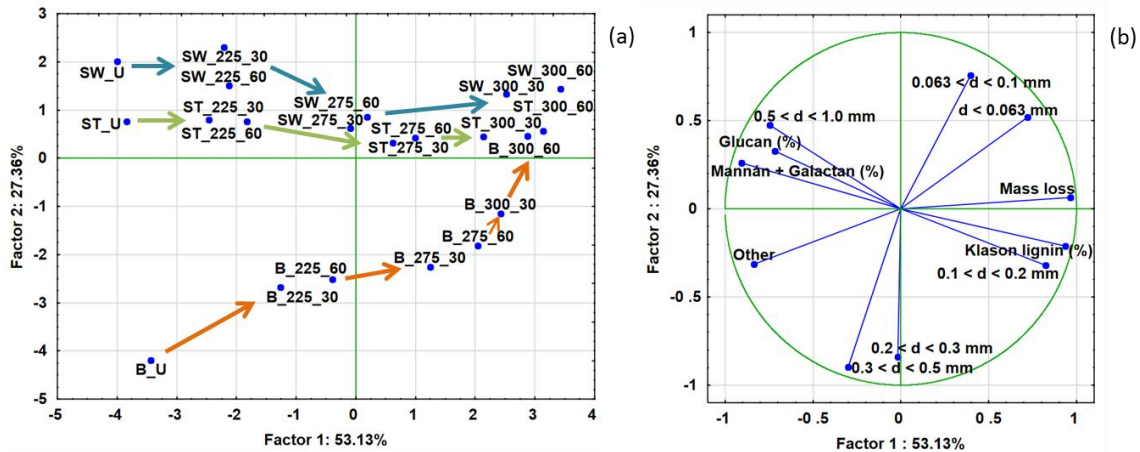


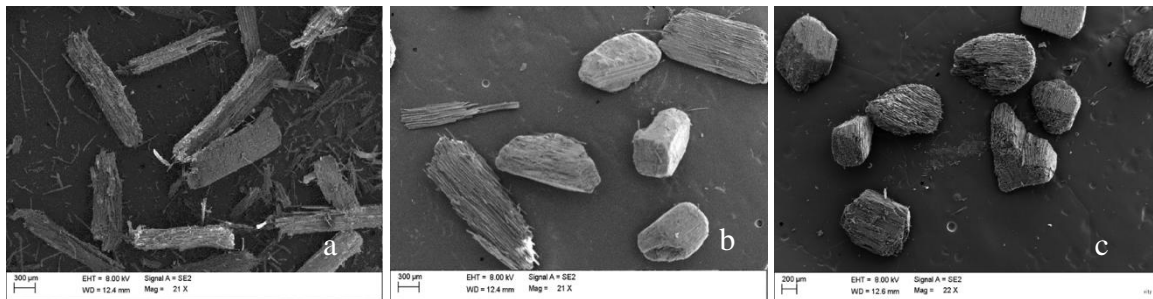
Fig. 6. Result of the principal component analysis based on the chemical composition and the particle size distribution data: (a) score and (b) loading plot. Score plot shows the studied samples in the space defined by the Factors. Factor loading denotes the correlation between original variables and the Factors. The arrows present the direction of the variation of the studied samples with increasing torrefaction severity. SW, stem wood; ST, stump; BA, bark; SW_U, untreated bark; SW_225_30, torrefied stump at 225°C for 30 minutes

3.6 SEM analysis

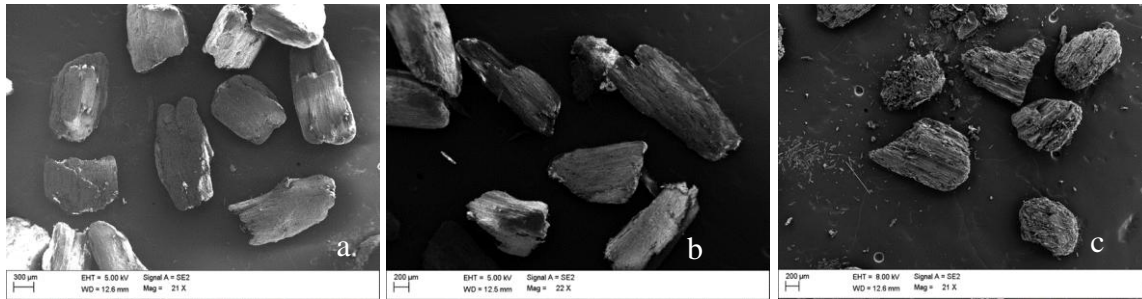
Scanning electron microscopy was used to investigate microstructure and morphology of untreated and torrefied stem wood, stump and bark. As shown in Fig. 4, the amount of ground stem wood and stump particles with size in the range $0.5 \text{ mm} < d < 1 \text{ mm}$ and $d < 0.063 \text{ mm}$ were changed substantially at torrefaction temperatures of 225 and 300 °C. Therefore, ground stem wood and stump particles in the two size ranges were examined by SEM. For comparison purpose, the ground bark particles in the same size range were studied.

Fig. 7-9 show SEM images of untreated and torrefied stem wood, stump and bark particles in the size range of $0.5 \text{ mm} < d < 1 \text{ mm}$. For the untreated stem wood, it contains a mixture of large and long particles and thin fibres as shown in Fig. 7a. One should note that it is the particle diameter (shortest dimension) that determines whether a particle can pass through a sieve with a certain cut-size. Fig. 7b displays that there is no evident change of particle diameters at a torrefaction temperature of 225 °C, but the particle lengths are reduced significantly compared to untreated stem wood particles shown in Fig. 7a. It means that more particles with smaller length-to-diameter ratios can

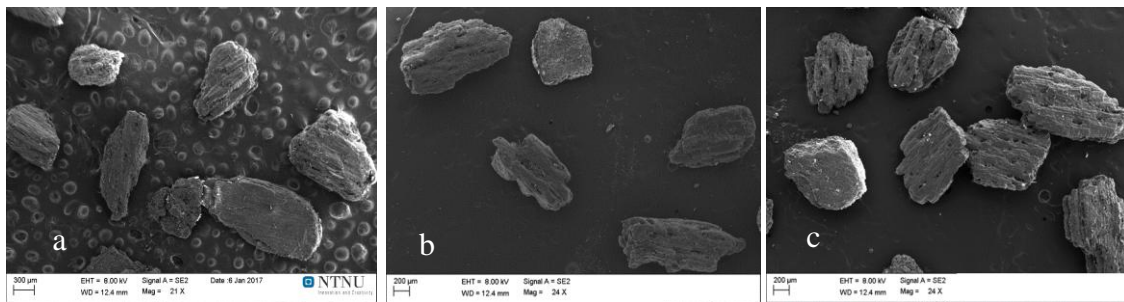
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4 pass through a sieve, explaining the percentage reduction of large particles displayed in
5 Figure 4. Additionally, with reduction of the length-to-diameter ratio, torrefied stem
6 wood particles become more spherical, which can consequently improve fluidisation
7 behaviours and conversion efficiency [12]. In the plant cell wall, the oriented cellulose
8 fibres are interlinked and bond by disoriented hemicellulose chains to form a
9 hemicellulose-cellulose matrix [12]. The combination of orientation of cellulose fibres
10 and their length is a main cause why the major fraction of ground woody biomass are
11 particles with needle shape and high length-to-diameter ratio. During torrefaction,
12 decomposition and depolymerisation of cellulose in the stem wood resulted in decrease of
13 cellulose fibres and length of ground particles consequently. Fig. 6c shows that, after
14 torrefaction at 300 °C, the ground stem wood particles are more porous with massive
15 pores and some open tubular structure. The later one is mainly due to decarbonisation and
16 destruction of lignin. The porous structure of the stem wood torrefied at 300 °C (Figs. 3
17 and 4) allows for the better grindability and lower energy consumption. Figs. 8 and 9
18 show that untreated stump and bark have different microstructure and morphology than
19 stem wood. Almost no thin fibres can be observed from Fig. 8a and Fig. 9a. In addition, it
20 can be seen that the length-to-diameter ratios of the particles shown in these images are
21 not large. It explains why rather small amounts of particles in this size range ($0.5 \text{ mm} < d$
22 $< 1 \text{ mm}$) were obtained from sieving tests, in comparison to results from stem wood. Fig.
23 8c displays that stump has porous structure with many pores and tubular openings. For
24 the bark, increasing torrefaction severity caused a number of openings and fissures on the
25 surface, which can be explained by the decomposition of polymeric compositions and
26 volatilisation of gas products. The porosity is most visible for the torrefied bark at 300 °C
27 and 60 minutes holding time, i.e. the most severe torrefaction condition.



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4 **Fig. 7.** SEM images of the ground particles ($0.5 \text{ mm} < d < 1 \text{ mm}$) from stem wood (a)
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6 minutes
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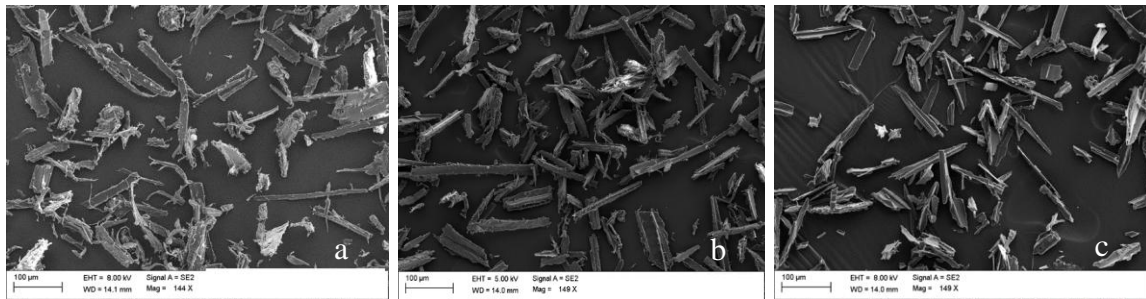
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20 **Fig. 8.** SEM images of the ground particles ($0.5 \text{ mm} < d < 1 \text{ mm}$) from (a) untreated stump, (b)
21 torrefied at 225°C with 60 minutes and (c) torrefied at 300°C with 60 minutes
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35 **Fig. 9.** SEM images of the ground particles ($0.5 \text{ mm} < d < 1 \text{ mm}$) from (a) untreated bark, (b)
36 torrefied at 225°C with 60 minutes and (c) torrefied at 300°C with 60 minutes
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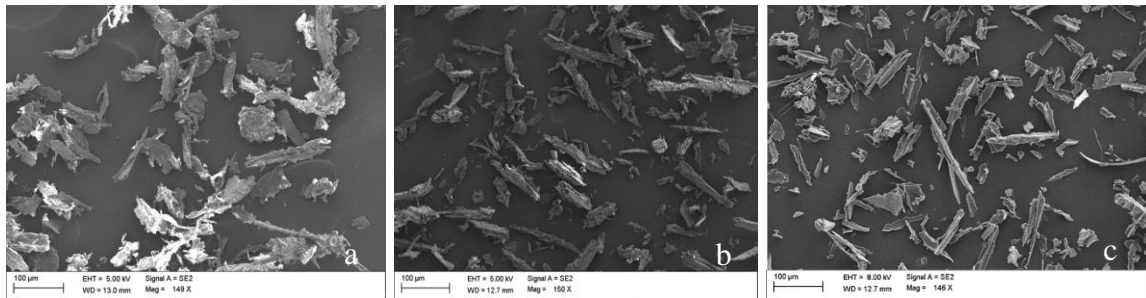
39 Figs. 10-12 show SEM images of untreated and torrefied stem wood, stump and bark
40 particles in the size range of $d < 0.063 \text{ mm}$. It is clearly seen that untreated wood has a
41 fibrous structure with large length-to-diameter ratios. After torrefaction, more isolated
42 particles are observed and no fibres can be seen. As reported in other studies, presence of
43 the fibres can cause linking and agglomeration of fine wood particles, which are also
44 more difficult to pass through the sieve openings [14]. It partially explains that only a
45 small amount of particles with size less than 0.063 mm were obtained from the sieving
46 test. On the other hand, particles from torrefied stem wood have much more smooth and
47 clean surfaces, compared to those from untreated stem wood. Additionally, more particles
48 with smaller length-to-diameter ratios can be observed in Figs. 10b and 10c. Hence, the
49 evident increase of fine particles shown in Fig. 4 can be explained by reduction of fibres
50 and particle length-to-diameter ratios. Fig. 11 shows that small untreated stump particles
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4 have similar structure as the stem wood, but with less fibres. With increase of torrefaction
5 severity, more particles with shorter length were produced as shown in Fig. 11c. The
6 small untreated bark particles have considerably smaller sizes and more spherical shape
7 compared to stem wood and stump. Compared to ground particles from bark torrefied at
8 225 °C (Fig. 12b), much more smaller particles can be observed (Fig. 12c). It agrees well
9 with the significant increase of the amount of the small particles obtained from the
10 sieving test (Fig. 4).
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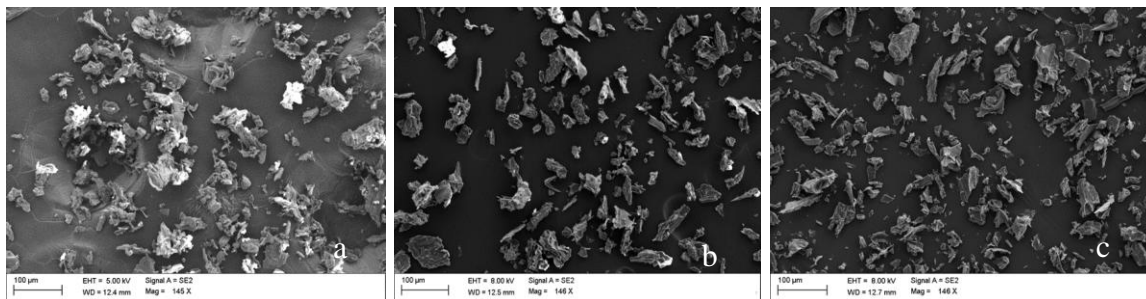
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Fig. 10. SEM images of the ground particles ($d < 0.063$ mm) from (a) untreated stem wood, (b) torrefied at 225°C with 60 minutes and (c) torrefied at 300°C with 60 minutes



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Fig. 11. SEM images of the ground particles ($d < 0.063$ mm) from (a) untreated stump, (b) torrefied at 225°C with 60 minutes and (c) torrefied at 300°C with 60 minutes



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4 **Fig. 12.** SEM images of the ground particles ($d < 0.063$ mm) from (a) untreated bark, (b)
5 torrefied at 225°C with 60 minutes and (c) torrefied at 300°C with 60 minutes
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8 **4 Conclusions**

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10 The effects of torrefaction on the physical properties, grindability and chemical
11 compositions and morphological structures of Norway spruce stem wood, stump and bark
12 were investigated. The results showed that torrefaction temperature and residence time
13 had effects on the grindability and chemical compositions of the studied biomass samples.
14 The torrefaction temperature had more significant effects on characteristics of the studied
15 biomass samples. Overall, the heating value and proximate and element compositions of
16 torrefied biomass samples improved compared to those of untreated biomasses. The
17 hemicellulose and cellulose contents of the torrefied biomass samples decreased with
18 increase of torrefaction severity, with increase of the lignin content accordingly. The
19 grindability of the stem wood and stump was significantly improved after the torrefaction
20 treatment. For the stem wood and stump torrefied at 225 °C, only approximately half of
21 the grinding energy was needed compared to grinding the dried raw feedstocks. In
22 addition, the coarse particles with sizes in the range of 0.5 to 1 mm were completely
23 removed after grinding when the stem wood and stump were torrefied at 275 °C. Much
24 less energy was required for grinding bark, and torrefaction did not affect the grinding
25 energy requirement significantly. The fraction of fine particles ($d < 0.063$ mm) increased
26 considerably in the ground torrefied bark. The improvement of grindability of torrefied
27 biomass samples can be partially explained by decomposition of the hemicellulose and
28 cellulose. It causes loss of strength and tenacity and makes particle size reduction more
29 easily, consequently. The SEM analyses revealed changes of morphological structures of
30 the studied biomass samples before and after torrefaction. For the stem wood and stump,
31 fibres and particles with large length-to-diameter ratios were substantially reduced after
32 torrefaction at increasing temperatures. For the particles from biomass samples torrefied
33 at 300 °C, they generally have more porous structure with observation of pores and
34 tubular openings on the surface.
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57 **Acknowledgements**

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Highlights:

- Comparative study of torrefied stem wood, stump and bark of Norway spruce
- Torrefaction cause increase of higher heating value, fixed carbon and energy density of studied woody biomasses
- Changes in chemical composition and improvement of grindability of torrefied samples
- Principal component analyses reveal statistical correlations between grindability and chemical compositions
- SEM analyses show torrefied sample particles having lower length-to-diameter ratios



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Professor Jinyue Yan, Editor-in-Chief
Applied Energy
KTH Royal Institute of Technology,
Stockholm, and Mälardalen University,
Västerås, Sweden

Dear Professor Jinyue Yan,

There is continuous increasing attention from exploiting and using low-grade biomass fuels from the forest sector. Torrefaction is an efficient way to upgrade these fuels for further efficient energy conversion purpose. In this submission, we studied effects of torrefaction on physicochemical characteristics and grindability of stem wood, stump and bark of Norway spruce. To the best of our knowledge, this is the first work reporting chemical composition analysis of untreated and torrefied stumps. In addition, detailed studies of change of physicochemical characteristics and grindability of stump and bark are presented.

My co-authors MSc. Eszter Barta-Rajnai, Dr. Øyvind Skreiberg, PhD. Roger Khalil, Dr. Zsuzsanna Czégény, Dr. Emma Jakab, PhD. Zsolt Barta, Dr. Morten Grønli, and I will be grateful for your consideration of our paper for publication in the Special Issue to ICAE 2016. I am the corresponding author and the submitter. Suggested keywords are: stem wood, stump, bark, torrefaction, grindability, chemical composition.

Thanks for your stewardship of one of the world's most prestigious and important technical journals!

Best regards
Liang Wang

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